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(54) Title: LOW MOLECULAR WEIGHT NITRILE RUBBER

(57) Abstract: The present invention relates to nitrile rubber polymers having lower molecular weights and narrower molecular weight distributions than those known in the art. Another object is a process for the manufacture of said nitrile rubber and the use of said nitrile rubber for the manufacture of shaped articles.

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Low Molecular Weight Nitrile Rubber

Field of the Invention.

The present invention relates to nitrile rubber polymers having lower
5 molecular weights and narrower molecular weight distributions than those
known in the art and a process for its manufacture.

Background of the Invention

Nitrile rubber (NBR), a co-polymer comprising at least one
10 conjugated diene, at least one unsaturated nitrile and optionally further
comonomers, is a specialty rubber which has good chemical resistance, and
excellent oil resistance. Coupled with the high level of mechanical properties
of the rubber (in particular the high resistance to abrasion) it is not surprising
that NBR has found widespread use in the automotive (seals, hoses, bearing
15 pads), electrical (cable sheathing), mechanical engineering (wheels, rollers)
and footwear industries, amongst others.

Commercially available NBR is manufacture by emulsion polymerization.
The monomers are emulsified in water, a free radical-generating catalyst is
added and the mixture is agitated whilst a constant temperature is maintained.
20 After the desired degree of polymerization is reached, a shortstop and
stabilizers are added to the reaction system causing termination of the
polymerization process. Generally, NBR obtained by this process has a
Mooney viscosity in the range of from 30 to 90, an Mw in the range of from
250,000 to 350,000, an Mn in the range of from 80,000 to 150,000 and a
25 polydispersity index greater than 3.2.

In addition, so-called "liquid NBR" having a very low Mooney viscosity
and a low molecular weight can be produced be adding the shortstop agent
early in the reaction process. As in the case of regular NBR, the resulting
liquid NBR has a polydispersity greater than 3.0.

30 Karl Ziegler's discovery of the high effectiveness of certain metal salts,
in combination with main group alkylating agents, to promote olefin
polymerization under mild conditions has had a significant impact on chemical

research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the proposed coordination-insertion mechanism but also effect an entirely different chemical process, that is the mutual exchange (or metathesis) reaction of alkenes according to a scheme as shown in Figure1.

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

Homogeneous systems have also been devised and used to effect olefin metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly known as Grubb's catalyst) has been widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents (C_6H_6 , CH_2Cl_2 , THF, *t*-BuOH).

The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. The most commonly-used catalysts are based on Mo, W and Ru. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer synthesis has allowed the preparation of new polymeric material with unprecedented properties (such as highly stereoregular polynorbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinylidimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl_6 and $SnMe_4$ or $PhC\equiv CH$ co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

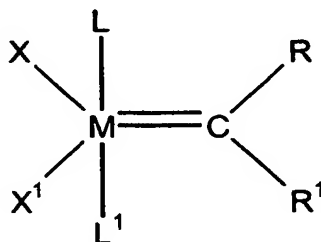
The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula $\{M(=NR_1)(OR_2)_2(=CHR)\}$; $M = Mo, W$ to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however, the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

Summary of the Invention

We have now discovered that a low molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis. Rubbers having a narrow molecular weight distribution have certain advantages over those having a broad molecular weight distribution, one of these being that they have improved physical properties, resulting, for example, in better processability of the rubber.

Thus, one aspect of the disclosed invention is a nitrile rubber having a molecular weight (M_w) in the range of from 25,000 to 200,000 g/mol, a Mooney viscosity (ML 1+4 @100 deg. C) of less than 25, and a MWD (or polydispersity index) of less than 2.5.

Another object of the invention is a process for the preparation of said nitrile rubber comprising the step of subjecting said nitrile rubber to a metathesis reaction in the presence of at least one co-olefin and at least one compound selected from the group consisting of compounds of the general formulas I, II, III or IV,



Formula I

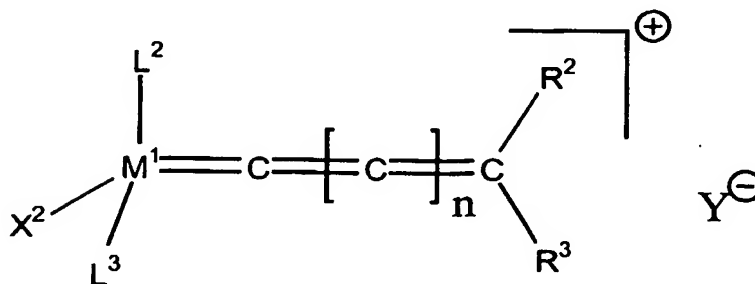
wherein:

M is Os or Ru;

R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X' are independently any anionic ligand; and

L and L¹ are independently any neutral ligand; optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand;



Formula II

5 wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-
 10 C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

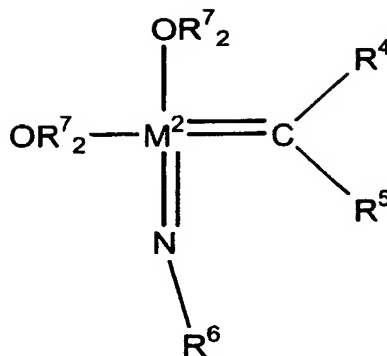
X² is an anionic ligand; and

L² is a neutral π -bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or
 15 polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups,
 20 phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y⁻ is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



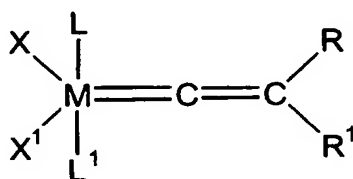
Formula III

wherein

M^2 is Mo or W

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the group consisting of $\text{C}_2\text{-C}_{20}$ alkenyl, $\text{C}_2\text{-C}_{20}$ alkynyl, $\text{C}_1\text{-C}_{20}$ alkyl, aryl, $\text{C}_1\text{-C}_{20}$ carboxylate, $\text{C}_1\text{-C}_{20}$ alkoxy, $\text{C}_2\text{-C}_{20}$ alkenyloxy, $\text{C}_2\text{-C}_{20}$ alkynyloxy, aryloxy, $\text{C}_2\text{-C}_{20}$ alkoxy carbonyl, $\text{C}_1\text{-C}_{20}$ alkylthio, $\text{C}_1\text{-C}_{20}$ alkylsulfonyl and $\text{C}_1\text{-C}_{20}$ alkylsulfinyl;

R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof;



Formula VI

wherein

M is Os or Ru;

R and R^1 are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl

X and X^1 are independently any anionic ligand; and

L and L^1 are independently any neutral ligand.

In still another aspect, the present inventions relates to the use of said nitrile rubber for the manufacture of a shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.

5

Description of the Invention

As used throughout this specification, the term "nitrile rubber" is intended to have a broad meaning and is meant to encompass a copolymer having repeating units derived from at least one conjugated diene, at least one
10 alpha,beta-unsaturated nitrile and optionally further one or more copolymerizable monomers.

The conjugated diene may be any known diene, in particular a C₄-C₆ conjugated diene. Preferred conjugated dienes are butadiene, isoprene, piperylene, 2,3-dimethyl butadiene or mixtures thereof. Even more preferred
15 C₄-C₆ conjugated diene are butadiene, isoprene and mixtures thereof. The most preferred C₄-C₆ conjugated diene is butadiene.

The alpha,beta-unsaturated nitrile may be any known alpha,beta-unsaturated nitrile, in particular a C₃-C₅- α,β -unsaturated nitrile. Preferred C₃-C₅ α,β -unsaturated nitriles are acrylonitrile, methacrylonitrile, ethacrylonitrile or
20 mixtures thereof. The most preferred C₃-C₅ α,β -unsaturated nitrile is acrylonitrile.

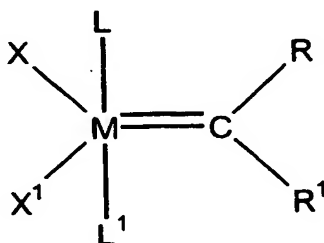
Preferably, the copolymer comprises in the range of from 40 to 85 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 15 to 60 weight percent of repeating units derived
25 from one or more alpha,beta-unsaturated nitriles. More preferably, the copolymer comprises in the range of from 60 to 75 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 25 to 40 weight percent of repeating units derived from one or more alpha,beta-unsaturated nitriles. Most preferably, the copolymer comprises in the range of
30 from 60 to 70 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 30 to 40 weight percent of repeating units derived from one or more alpha,beta-unsaturated nitriles.

Optionally, the copolymer may further comprise repeating units derived from one or more copolymerizable monomers, such as unsaturated carboxylic acids. Non-limiting examples of suitable unsaturated carboxylic acids are fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof.

- 5 Repeating units derived from one or more copolymerizable monomers will replace either the nitrile or the diene portion of the nitrile rubber and it will be apparent to the skilled in the art that the above mentioned figures will have to be adjusted to result in 100 weight percent. In case of the mentioned unsaturated carboxylic acids, the nitrile rubber preferably comprises repeating
- 10 units derived from one or more unsaturated carboxylic acids in the range of from 1 to 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

- Other preferred optionally further monomers are unsaturated mono- or di-carboxylic acids or derivatives thereof (e.g., esters, amides and the like)
- 15 including mixtures thereof.

The inventive process is conducted in the presence of one or more compounds of the general formulas I, II, III or IV,



Formula I

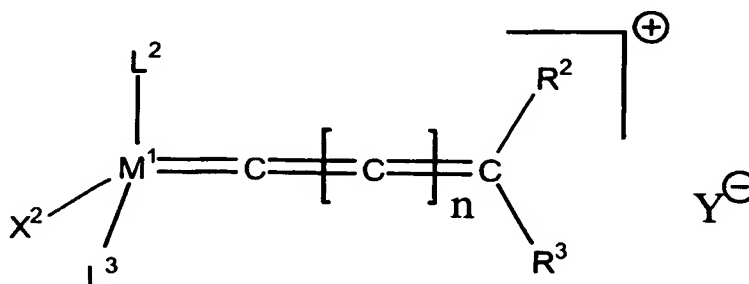
- 20 wherein

M is Os or Ru;

- R and R¹ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-
- 25 C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X¹ are independently any anionic ligand; and

L and L¹ are independently any neutral ligand, such as phosphines, amines, thioethers or imidazolidines or any neutral carbene, optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand;



Formula II

wherein

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

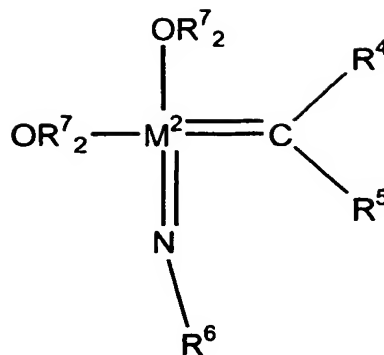
X² is an anionic ligand; and

L² is a neutral π -bonded ligand, preferably arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



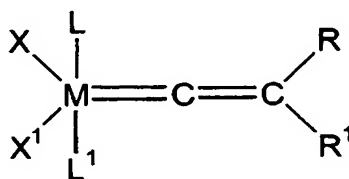
Formula III

wherein

M^2 is Mo or W

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxy carbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl;

R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof;



Formula VI

wherein

M is Os or Ru;

R and R^1 are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl

X and X^1 are independently any anionic ligand; and

L and L¹ are independently any neutral ligand, such as phosphines, amines, thioethers or imidazolidines or any neutral carbene, optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand.

Compounds of Formula I are preferred. Compounds of Formula I wherein L and L¹ are trialkylphosphines, X and X¹ are chloride ions and M is Ruthenium are even more preferred.

The amount of compounds will depend upon the nature and catalytic activity of the compound(s) in question. Typically, the ratio of compound(s) to NBR is in the range of from 0.005 to 5, preferably in the range of from 0.025 to 1 and, more preferably, in the range of from 0.1 to 0.5.

The metathesis reaction is carried out in the presence of a co-olefin which is a C₁ to C₁₆ linear or branched olefin such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is preferably in the range of from 1 to 200 weight %. Where the co-olefin is a gas (such as ethylene), the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from 1 * 10⁵ Pa to 1 * 10⁷ Pa, preferably in the range of from 5.2 * 10⁵ Pa to 4 * 10⁶ Pa.

The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from 1 to 20% by weight, most preferably in the range of from 6 to 15% by weight.

The inventive process usually is carried out at a temperature in the range of from 20 to 140°C; preferably in the range of from 60 to 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which

the reaction is performed. The metathesis usually is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity. Whenever referenced throughout the specification the molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millennium software version 3.05.01. Samples were dissolved in tetrahydrofuran (THF) stabilized with 0.025% BHT. The columns used for the determination were three sequential mixed-B gel columns from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

The Mooney viscosity of the rubber was determined using ASTM test D1646.

The inventive nitrile rubber is very well suited for the manufacture of a shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.

EXAMPLES**Examples 1-4**

5 Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene and monochlorobenzene (MCB) were purchased from Alfa, Aldrich Chemicals, and PPG respectively and used as received.

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

10	Cement Concentration	6 or 15% by weight
	Co-Olefin	Ethylene or 1-Hexene
	Co-Olefin Concentration	see Table A
	Agitator Speed	600 rpm
	Reactor Temperature	see Table A
15	Catalyst Loading	see Table A
	Solvent	Monochlorobenzene
	Substrate	statistical Butadiene-acrylonitrile copolymer with a acrylonitrile content of 34 mol% and a
20		Mooney-Viscosity ML (1+4)@ 100 deg. C of 35

The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The reactor was pressurized to the desired ethylene pressure for
 25 examples 1-3 or to 100psi of Nitrogen for example 4. The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration,
 30 the reaction was assumed to be complete after 18 hours.

Example 1: Details

75g of rubber was dissolved in 1175g of MCB (6 wt.-% solid). The cement was then charged to the reactor and degassed 3 times with C₂H₄ (6.9 * 10⁵ Pa) under full agitation.

Example 2: Details

200g of rubber was dissolved in 1133g of MCB (15 wt.-% solid). The cement was then charged to the reactor and degassed 3 times with C₂H₄ (6.9 * 10⁵ Pa) under full agitation.

Example 3: Details

450g of rubber was dissolved in 2550g of MCB (15 wt.-% solid). The cement was then charged to the reactor and degassed 3 times with C₂H₄ (6.9 * 10⁵ Pa) under full agitation.

Example 4: Details

75g of rubber was dissolved in 1175g of MCB (6 wt.-% solid). The cement was then charged to the reactor. 20g of 1-hexene was added to the reactor and the mixture was degassed 3 times with dry N₂ under full agitation.

Table A Experimental Details

	Example 1	Example 2	Example 3	Example 4
Cement conc.	6	15	15	6
Co-olefin	C ₂ H ₄	C ₂ H ₄	C ₂ H ₄	1-hexene
co-olefin conc.	400 psi	500 psi	500 psi	20g
Reactor temp.	80°C	80°C	80°C	80°C
Catalyst load	0.25	0.25	0.05	0.25

For a typical product the Mn is 30 kg/mole (compared to 85 kg/mole for the starting polymer) whilst the Mw is 55 kg/mole (compared to 300 kg/mole for the starting polymer). As can be seen from Table 1, however, higher molecular weights (Mw) can also be obtained by manipulation of the experimental conditions (for example by lowering the catalyst loading). As expected, the molecular weight distribution falls from 3.5 for the substrate (starting polymer) to 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

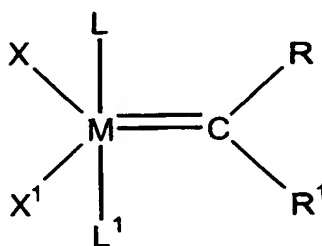
A summary of the polymer properties for selected samples is shown in Table 1. The GPC results show up to a fivefold reduction in Mw and a narrowing of the polydispersity index to 2.0.

Table 1 Summary of Polymer Properties

	MN	MW	MZ	PDI	Mooney Viscosity (ML 1+4 @ 100 deg. C)
substrate	85000	296000	939000	3.50	35
Experiment 1	27000	54000	92000	2.00	2.5
Experiment 2	32000	66000	117000	2.06	-
Experiment 3	71000	180000	455000	2.5	
Experiment 4	40000	84000	154000	2.1	-

Claims

1. A nitrile rubber having a molecular weight (M_w) in the range of from 25,000 to 200,000 g/mol, a Mooney viscosity (ML 1+4 @100 deg. C) of less than 25 and a polydispersity index of less than about 2.5.
2. A nitrile rubber according to claim 1, wherein the nitrile rubber comprises in the range of from 40 – 80 wt% of repeating units derived from at least one conjugated diene and in the range of from 15 - 60 wt% of repeating units derived from at least one alpha,beta-unsaturated nitrile.
3. A nitrile rubber according to claim 2, wherein the nitrile rubber further comprises one or more further co-monomers and wherein the wt%. for the repeating units derived from diene(s) and nitrile(e) are adjusted to result in 100 wt% in total.
4. A nitrile rubber according to claim 3, wherein the co-monomers are one or more unsaturated carboxylic acids.
5. A process for the preparation of a nitrile rubber comprising the step of subjecting said nitrile rubber to a metathesis reaction in the presence of at least one co-olefin and at least one compound selected from the group consisting of compounds having the formula I, II, III or IV



Formula I

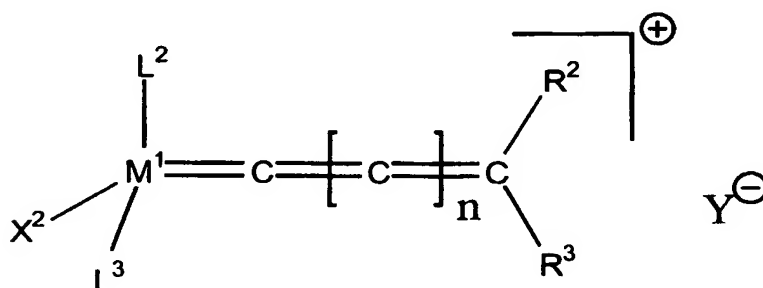
wherein

M is Os or Ru,

R and R¹ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl,

X and X¹ are independently any anionic ligand, and

L and L¹ are independently any neutral ligand; optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand;



Formula II

wherein

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl,

X² is an anionic ligand,

L² is a neutral π -bonded ligand independent of whether they are mono- or polycyclic,

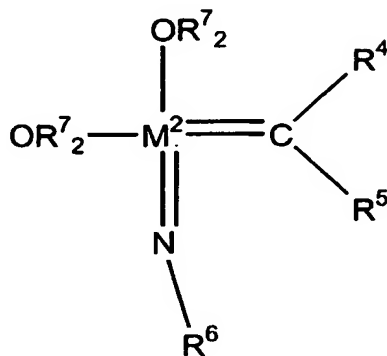
L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites,

phosponites, phosphinamines, arsines, stibenes, ethers,
amines, amides, imines, sulfoxides, thioethers and pyridines,

Y^- is a non-coordinating anion,

n is an integer in the range of from 0 to 5;

5



Formula III

wherein

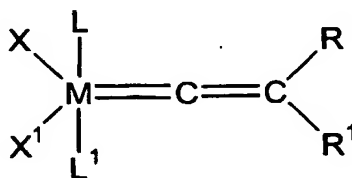
M^2 is Mo or W,

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the
group consisting of C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkyl,
aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20}
alkynyloxy, aryloxy, C_2 - C_{20} alkoxycarbonyl, C_1 - C_{20} alkylthio, C_1 -
 C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl,

R^6 and R^7 are independently selected from any unsubstituted or halo-
substituted alkyl, aryl, aralkyl groups or silicon-containing analogs
thereof,

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Formula VI

wherein

M is Os or Ru,

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R and R¹ are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl,

X and X¹ are independently any anionic ligand and

L and L¹ are independently any neutral ligand.

6. A process according to claim 5 wherein a compound of Formula I is present.

7. A process according to claim 6 wherein L and L¹ are trialkylphosphines, X and X¹ are chloride ions and M is ruthenium.

8. A process according to claim 5 wherein the co-olefin(s) is/are a C₂ to C₁₆ linear or branched olefin(s).

9. A process according to claim 8 wherein the co-olefin is selected from the group consisting of ethylene and 1-hexene.

10. A process according to claim 5 wherein the process is carried out in an inert solvent selected from the group consisting of monochlorobenzene, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone and cyclohexane.

11. A process according to claim 5 wherein the concentration of nitrile rubber is in the range of from 1 to 40% by weight.

12. The use of a nitrile rubber according to any of the claims 1-4 in the manufacture of a shaped article

13. The use according to claim 12 wherein the shaped article is a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.

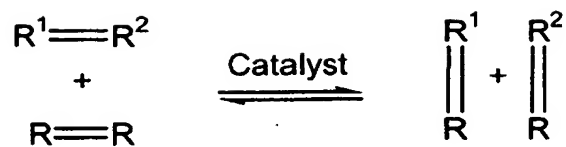


Figure 1

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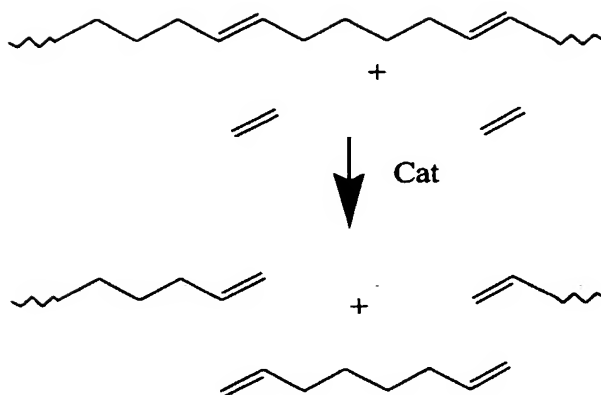


Figure 2

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 02/00965

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08C19/08 C08F8/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	WO 96 04289 A (CALIFORNIA INSTITUTE OF TECHNOLOGY) 15 February 1996 (1996-02-15) claims 1-25; example 10 ---	1-13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

4 October 2002

Date of mailing of the international search report

14/10/2002

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 02/00965

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A	WO 97 06185 A (CALIFORNIA INSTITUTE OF TECHNOLOGY) 20 February 1997 (1997-02-20) page 7, line 7 - line 12; claims 1-42 ----	1
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